

FINAL REPORT

Biodegradable Sonobuoy Decelerators

ESTCP Project WP-201222

JUNE 2015

Warren Ingram
Naval Air Warfare Center Weapons Division

Chris Thellen
Jo Ann Ratto Ross
**Natick Soldier Research and Development
Engineering Center**

Brandon Swope
Space and Naval Warfare Systems Center, Pacific

Susan Lang
Naval Facilities Engineering Command – Atlantic

Distribution Statement A

This document has been cleared for public release



REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 08-06-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) Jan 2012 – Sep 2013	
4. TITLE AND SUBTITLE Biodegradable Sonobuoy Decelerators			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Warren Ingram, Chris Thellen, Jo Ann Ratto Ross, Brandon Swope, and Susan Lang			5d. PROJECT NUMBER ESTCP WP-201222		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Weapons Division, China Lake, CA Natick Soldier Research and Development Engineering Center, Natick, MA Space and Naval Warfare Systems Command, San Diego, CA Naval Facilities Engineering Command Atlantic, Norfolk, VA			8. PERFORMING ORGANIZATION REPORT NUMBER WP-201222		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of Defense Environmental Security Technology Certification Program, Washington, D.C.			10. SPONSOR/MONITOR'S ACRONYM(S) ESTCP		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT NAVAIR Public Release 15-02-08 Distribution Statement A – “Approved for public release; distribution is unlimited”					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT In response to environmental concerns regarding nylon decelerators from sonobuoys polluting the oceans and negatively impacting a wide variety of ocean life, a multi-agency proposal was presented to ESTCP to replace the nylon with a biodegradable material. Two materials studied were polyvinyl alcohol (PVOH) and polyhydroxyalkanoate (PHA). Single and multilayered PVOH films were evaluated as well as a coarse composite weave of PVOH/PHA film strips and a weave of PHA film strips. A suitable replacement material was not quite matured to the readiness point for technology transition.					
15. SUBJECT TERMS biodegrade, decelerator, sonobuoy, polyvinyl alcohol, polyhydroxyalkanoate, marine environment					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as report	18. NUMBER OF PAGES 35	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code)

Table of Contents

1.0 INTRODUCTION	1
1.1 BACKGROUND	1
1.2 OBJECTIVE OF THE DEMONSTRATION	1
1.3 REGULATORY DRIVERS	1
2.0 DEMONSTRATION TECHNOLOGY	2
2.1 TECHNOLOGY DESCRIPTION	2
2.2 TECHNOLOGY DEVELOPMENT	2
2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY	5
2.4 EXPECTED APPLICATIONS OF THE TECHNOLOGY	6
3.0 PERFORMANCE OBJECTIVES	7
4.0 TEST DESIGN	8
4.1 LABORATORY TESTING.....	8
4.2 FIELD TESTING.....	11
5.0 PERFORMANCE ASSESSMENT	13
5.1 LABORATORY TEST RESULTS	13
5.2 FIELD TEST RESULTS	17
6.0 IMPLEMENTATION ISSUES	20
7.0 REFERENCES	21
APPENDIX A: POINTS OF CONTACT	22
APPENDIX B: STRENGTH TEST RESULTS FOR 6-MIL LAMINATED PVOH	23

List of Figures

Figure 1: Molecular Structure of PVOH (left) and PHA (right).....	2
Figure 2: Decelerator in Flight (left) and Ground Wind Inflation (right).....	3
Figure 3: Biodegradation of PHA Lid Material in Seawater after 3 Months of Immersion	3
Figure 4: Biodegradation of PHA and Glucose Materials (ASTM D6691)	4
Figure 5: Bioassay in Progress for Topsmelt.....	8
Figure 6: PVOH Dissolving in Sea Water	9
Figure 7: PVOH Tensile Test Setup (left) and Water Exposure Test (right).....	10
Figure 8: Details of PHOH/PHA Weave In-Process	10
Figure 9: Square Design for Decelerator	11
Figure 10: Test Vehicle and Decelerator	12
Figure 11: The Effect of Water Temperature and the Presence of Salt on the Disintegration Time of MonoSol A200 PVOH.....	14
Figure 12: Tensile Test Results of A200 6-mil Film Samples in Lengthwise (upper) and Transverse (lower) Rolled Directions	15
Figure 13: Effect of Water Exposure on Film Sample Held with 25-Pound Load.....	16
Figure 14: Simple Inflation Test of Prototype PHA Decelerator	17
Figure 15: Folded 6-Mil Thick PVOH Film Decelerator	18
Figure 16: Post Test Photograph of Top Surface of Square Decelerator.....	19
Figure 17: Post Test Photograph of Under Surface of Square Decelerator	19

List of Tables

Table 1: Material Properties of Mirel™ P4001 Film/Sheet Grade PHA.....	5
Table 2: Performance Objectives	7

List of Acronyms and Symbols

ASTM	American Society for Testing and Materials
DOC	dissolved organic carbon
DOD	Department of Defense
DON	Department of Navy
EIS	environmental impact statement
ESA	Endangered Species Act
ESTCP	Environmental Security Technology Certification Program
FED STD	Federal Standard
LC ₅₀	50 percent lethal concentration
mil	1/1000 of an inch
mg/L	milligrams per liter
NAWCWD	Naval Air Warfare Center Weapons Division
NSRDEC	Natick Soldier Research and Development Engineering Center
NGO	non-governmental organizations
NOAA	National Oceanic and Atmospheric Administration
PHA	polyhydroxyalkanoate
PIA	Parachute Industry Association
PVOH	polyvinyl alcohol
SPAWARS	Space and Naval Warfare Systems Command
VIMS	Virginia Institute of Marine Science
VOC	volatile organic compound
WHOI	Woods Hole Oceanographic Institution

Acknowledgments

The authors thank Dr. Robert Whitehouse, formerly of Metabolix, Inc. for his expertise in biodegradable polymers and for supplying sample materials for test and evaluation. We thank Tom Fetherston, Naval Undersea Warfare Center, and George Hart, Navy Region Northwest, for their valuable insights into protecting the marine environment. We are grateful to Andrew Strzepek and Christine Charette, Natick Soldier Research and Development Engineering Center, for their accomplishments in prototyping decelerator designs and conducting the airdrops. We greatly appreciate the decelerator expertise provided by Elsa Hennings, Naval Air Warfare Center, Weapons Division, and the decelerator background provided by David SeEVERS, Naval Air Warfare Center, Aircraft Division. We would also like to thank the Environmental Security Technology Certification Program for providing the funding for this work, and for program guidance from both Bruce Sartwell and Dr. Robin Nissan, ESTCP program managers for Weapon Systems and Platforms.

Executive Summary

In response to environmental concerns regarding nylon decelerators from sonobuoys polluting the oceans and negatively impacting a wide variety of ocean life, a multi-agency proposal was presented to ESTCP to replace the nylon with a biodegradable material. The two materials presented were polyvinyl alcohol (PVOH) and polyhydroxyalkanoate (PHA). Single and multilayered PVOH films were evaluated as well as a coarse composite weave of PVOH/PHA film strips and a weave of PHA film strips. During the initial phase of the project, material optimization, several problems were encountered which prevented demonstration of the decelerator. A suitable replacement material was not quite matured to the readiness point for technology transition. The project was subsequently canceled due to schedule constraints and technology maturity. Results and shortcomings of the effort are presented.

1.0 INTRODUCTION

1.1 BACKGROUND

The Navy uses thousands of sonobuoys world-wide annually for testing, training, and operations. These sonobuoys utilize a non-degradable rip-stop nylon decelerator for deployments from aircraft. During reviews of Navy at-Sea training Environmental Impact Statements (EISs), there were concerns from Federal Regulators, Non-Governmental Organizations (NGOs), and the public about the long-term effects of expended sonobuoy decelerators. In line with Department of Defense (DOD) and Department of Navy (DON) green initiatives, a project was proposed to continue testing and evaluation of dissolvable, biodegradable material that would minimize cumulative impacts from sonobuoy decelerators. The project was proposed by individuals from six different government agencies and one industry partner.

1.2 OBJECTIVE OF THE DEMONSTRATION

A proposal was presented to ESTCP in October 2011 to replace the traditional nylon sonobuoy decelerator textile materials with a film material of polyvinyl alcohol (PVOH) or a blend of PVOH with polyhydroxyalkanoate (PHA). The proposed film would disintegrate, dissolve, and eventually biodegrade to prevent long-term effects on marine life. Ensuring no toxicity of the film material in the marine environment was also part of the proposal. The demonstration goal was to qualify new decelerators for service in future sonobuoy production.

1.3 REGULATORY DRIVERS

The environmental concerns associated with nylon sonobuoy decelerators and their relevant regulatory drivers include: entanglement of and ingestion by marine mammals and sea turtles (Endangered Species Act [ESA]), as well as damaging or smothering benthic resources such as coral (ESA) and Essential Fish Habitat (Magnuson – Stevens Fishery Conservation and Management Act).

2.0 DEMONSTRATION TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

PVOH based film was evaluated as a material to replace traditional nylon woven fabric used to construct sonobuoy decelerators. PVOH is a non-toxic, water soluble synthetic polymer. When PVOH film is submersed in water, it will dissolve at rates that are directly related to water temperature, salinity and agitation rate. Figure 1 depicts the molecular structures of PVOH and PHA.

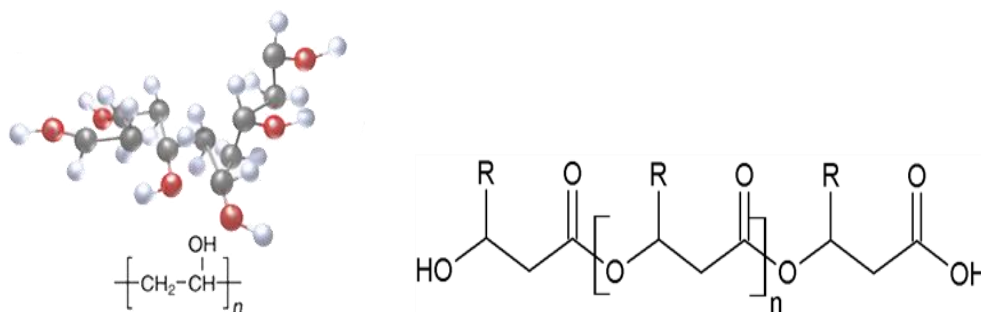


Figure 1: Molecular Structure of PVOH (left) and PHA (right).

PHA based film was also evaluated to determine suitability to replace nylon. It is a non-toxic polymer derived from bacterial fermentation of sugars and is marine biodegradable but not water soluble. PHA materials are some of the most highly marine biodegradable polymers that are thermoplastic and can be formed into film, sheet, and fiber using conventional melt-extrusion operations. Several grades have been commercialized and have received both U.S. and European certification as biodegradable in many environments including water, compost and soil. For example, Mirel P4001TM, a Metabolix, Inc. PHA product was awarded a certificate to use the “OK Biodegradable Water” conformity mark by AIB-VINCOTTE International. Reference [1].

2.2 TECHNOLOGY DEVELOPMENT

Prior to the initiation of the ESTCP project, several materials were evaluated by NSRDEC. The most promising materials evaluated in terms of performance and cost were PVOH and PHA films.

A prototype decelerator was constructed from PVOH film. Because the material properties for the PVOH film are not identical to the woven nylon fabric, the decelerator design had to be modified. Proof of concept tests were successfully conducted in 2010 using the prototype design (Figure 2).



Figure 2: Decelerator in Flight (left) and Ground Wind Inflation (right).

Toxicity of the PHA material has been studied in the marine environment. The Environmental Protection Agency's Polytox Test for toxicity was also performed for many PHA grades at NSRDEC as part of the ASTM Specification D7081 Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment. Results showed that no PHA grades were toxic to the marine environment. Extensive marine biodegradation testing of PHA materials have been conducted throughout the years at NSRDEC and Woods Hole Oceanographic Institution (WHOI), and an inter-laboratory effort coordinated by NSRDEC and WHOI was recently conducted with Algalita Marine Research Institute in California, Whitney Laboratories in Florida and the University of Rhode Island using NSRDEC's newest developed ASTM test, D7473, Test Method for Weight Attrition of Plastic Materials in the Marine Environment by Open System Aquarium Incubations. Metabolix Inc. has also done independent studies using end items as shown in Figure 3. Figure 3 depicts a cap-material made of PHA resin from Metabolix Inc. that was tested in the waters off the coast of St. Augustine, Florida at Whitney Laboratories. This material is much thicker than the parachute canopy and shows a weight loss of 55% after 3 months immersion in seawater. After 6 months of immersion, no sign of the material was found.



Figure 3: Biodegradation of PHA Lid Material in Seawater after 3 Months of Immersion.

Along with weight loss experiments such as this, marine biodegradation testing of these materials in accordance with ASTM D6691 "Standard Test Method for Determining Aerobic Biodegradation of Plastics Materials in the Marine Environment by a Defined Microbial

Consortium or Natural Seawater Inoculum” has been published. Figure 4 illustrates an example of this testing using several different grades of PHA as compared to a glucose positive control. Reference [2]. The graphs in Figure 4 illustrate that several grades of PHA reached greater than 80% mineralization (biodegradation) in 100 days. This test measures the conversion of elemental carbon to carbon dioxide and is a true measure of the biodegradation of a polymer vs. a stand-alone weight loss test. Biodegradation rates as high as these are rare for plastics in the marine environment due to cold temperatures, high hydrostatic pressure, and low microbial populations as compared to more favorable biodegradation environments such as compost.

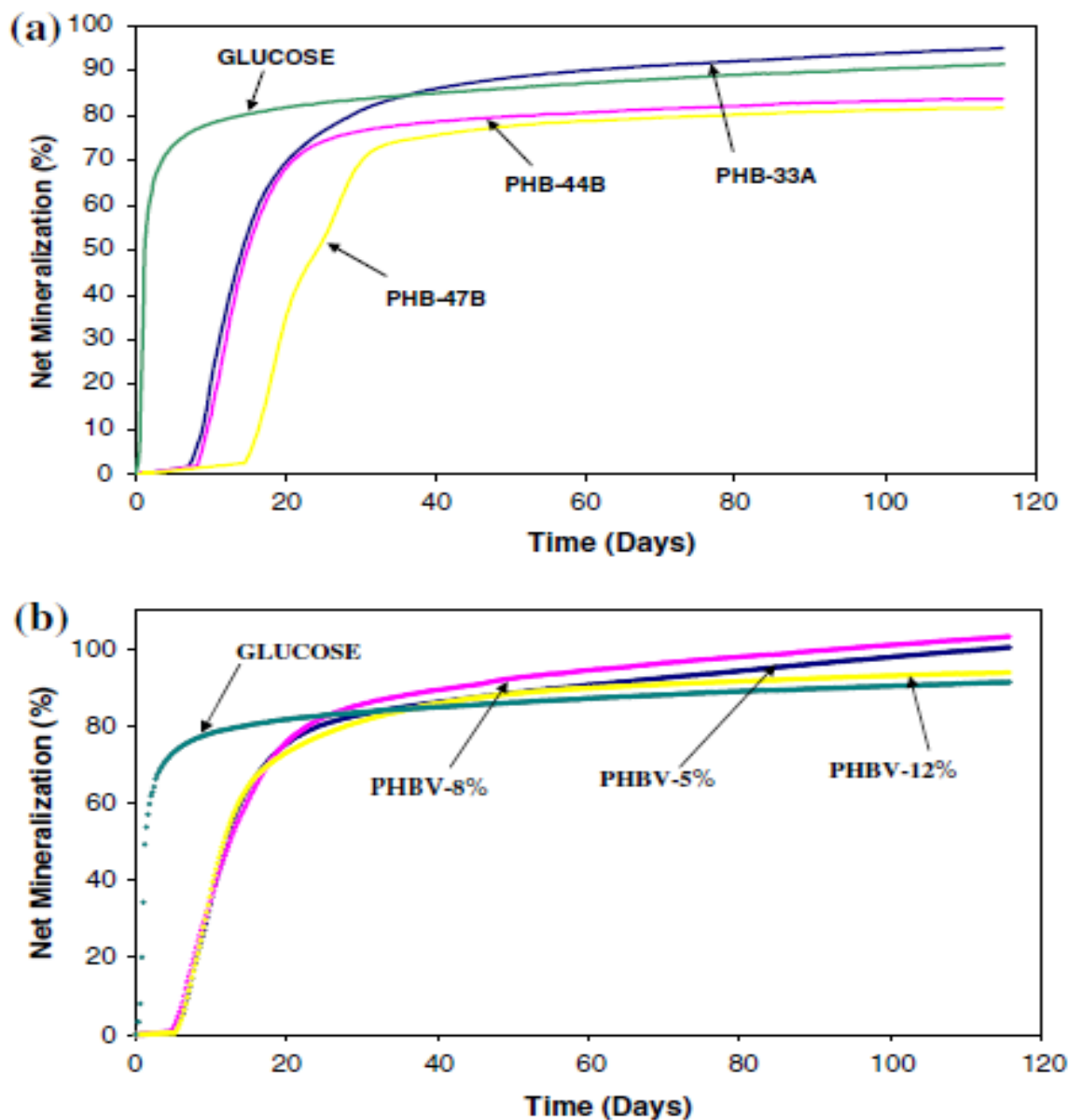


Figure 4: Biodegradation of PHA and Glucose Materials (ASTM D6691).

Research and developmental efforts in PHA applications have been supported by many organizations and, in particular, many applications requiring marine biodegradation. This effort in developing sonobuoy decelerators using PHA is supported by research efforts by the National Oceanic and Atmospheric Administration (NOAA) and the Virginia Institute of Marine Science (VIMS). These groups are currently examining PHA materials for use as biodegradable panels in fishing traps to reduce mortality in lost gear. Reference [3]. The biodegradation rates observed in their testing supports the earlier findings and demonstrates this material will biodegrade in numerous environments to which a sonobuoy decelerator would be subjected. There is significant interest from a variety of trap fisheries (e.g., lobster, stone crab, Dungeness crab) in the use of biodegradable panels.

Presented in Table 1 are mechanical properties of a film/sheet grade of PHA from Metabolix which was investigated for use in the decelerator.

Table 1: Material Properties of Mirel™ P4001 Film/Sheet Grade PHA.

Property	ASTM Method	Value
Tensile Strength at Yield	D638	2900 Psi
Tensile Elongation at Break	D638	5%
Flexural Modulus	D790A	275kpsi
Notched Izod	D256A	0.7ft-lbs/inch

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

A dissolving PVOH parachute would reduce smothering impacts to benthic resources and ingestion risk to marine mammals and sea turtles. Based on the attainable dissolution rate, minimal, if any, risk of entanglement/ingestion would remain. Upon future implementation of the biodegradable parachutes, studies would not be required to determine the direct and cumulative impacts of parachutes on benthic communities and ESA species. The dissolving nature of the PVOH material will cause concern when implementing the decelerator canopy in wet/humid conditions where mechanical strength may be altered by moisture.

Current limitations of the PHA technology include the non-availability of PHA material in woven product form as well as the length of time required for biodegradation. Current commercially available volumes of PHA are much lower than the nylon materials used in the sonobuoy decelerator and more expensive. Although biodegradable, PHA is not water soluble and will therefore require time to break apart into smaller fragments upon entering the ocean and beginning the biodegradation process.

2.4 EXPECTED APPLICATIONS OF THE TECHNOLOGY

Besides use in sonobuoy decelerators, this dissolving and biodegradable material technology could be leveraged to provide benefits to other DOD efforts, such as the need for discreet small scale aerial delivery operations. It could also be used in aerial delivery applications of bait for eradication of nuisance species by the U. S Department of Agriculture.

3.0 PERFORMANCE OBJECTIVES

Performance objectives for the project are summarized in Table 2.

Table 2: Performance Objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Material Strength	<ul style="list-style-type: none"> Strength and elongation test data collected on samples tested using FED-STD-191 and ASTM D5034 as guides. 	Meet or exceed 85-lb/in strength of PIA-C-7350 for Type I nylon cloth	Not met
Toxicity	<ul style="list-style-type: none"> Dilution tests for toxicity (mysid, topmelt, sea urchin and mussel) 	Non-toxic to sea life	Met for PVOH and PHA film, Not met for PVOH multi-layer
Dissolution in Salt Water (Reduce Smothering Hazard)	<ul style="list-style-type: none"> Laboratory test and observation 	Dissolve or break into pieces within 30 minutes (warm water) and 12 hours (cold water)	Met for PVOH, not met for PHA
Biodegradation	<ul style="list-style-type: none"> Tests using ASTM D7081 as a guide 	No adverse effect on sea life	Met for PHA film (by similarity)
Decelerator Stowage Volume	<ul style="list-style-type: none"> Packing trials 	Fit within existing design allocation	PVOH 6-mil: Not met PHA Weave: Not Tested
Rain Resistance During Deceleration Descent	<ul style="list-style-type: none"> Water exposure trials 	Retain adequate strength for time duration per operation requirements	PVOH: Not met PHA: Not tested
Cost	<ul style="list-style-type: none"> Analysis 	Comparable to nylon, under \$10.00 per unit	Unknown
Storage	<ul style="list-style-type: none"> Environmental Exposure and artificial aging (MIL-STD-810 as a guide) 	5-years with no degradation	Not Tested
Decelerator Performance	<ul style="list-style-type: none"> System Level Qualification Test Data Descent Rate Oscillation 	Meet all operational requirements	Not Tested

4.0 TEST DESIGN

4.1 LABORATORY TESTING

4.1.1 Toxicity tests

Toxicity testing was conducted at SPAWAR. Toxicity testing with mysids (shrimp) was conducted using a 96-hour survival test with eight different concentrations of PVOH solution in seawater: 0, 5, 10, 20, 40, 60, 80, and 100% of the PVOH stock solution. The solution was created by placing 6 grams of the PVOH film (cut into 1 cm² pieces) into 6 liters of filtered sea water. This was put on a stirrer for 72 hours. The solution was then filtered through a 0.45µm filter, and this is considered the 100% solution. Dissolved organic carbon (DOC) was used as a proxy for how much material was dissolved in seawater, as there currently is no analytical test for PVOH. Samples of the various dilutions were sent out for analysis of DOC with results presented as mg/L DOC-PVOH. Similar toxicity tests were also conducted for topsmelt, sea urchin and mussel (Figure 5). All tests were repeated for the laminated PVOH films.



Figure 5: Bioassay in Progress for Topsmelt.

4.1.2 Dissolution tests

Dissolution tests were conducted by placing material samples into beakers of either fresh or salt-water at various temperatures (5°C, 10°C, 15°C, and 20°C) and then agitating (Figure 6).



Figure 6: PVOH Dissolving in Sea Water.

4.1.3 Strength and Elongation Tests

Samples were cut from the films into 1-inch wide strips with a length of 9 inches. Using FED-STD-191 (Federal Test Method Standard, Textile Test Methods) as a guide, tests were conducted using an Instron tensile test machine at a rate of 12 inches per minute. Samples in both the rolled and transverse directions were tested. To understand the effect of rain on the material strength while the decelerator is descending through the atmosphere, 1-inch wide samples were tensile tested while being sprayed using a hand-operated bottle filled with room temperature tap water. Each side of the sample was sprayed every ten seconds. At the same time, the samples were loaded with a 25-pound load. The setups are depicted in Figure 7.

The PVOH/PHA and PHA woven cloths were manufactured using a manually operated loom (Figure 8). Samples were tensile tested using the same method as for the films.

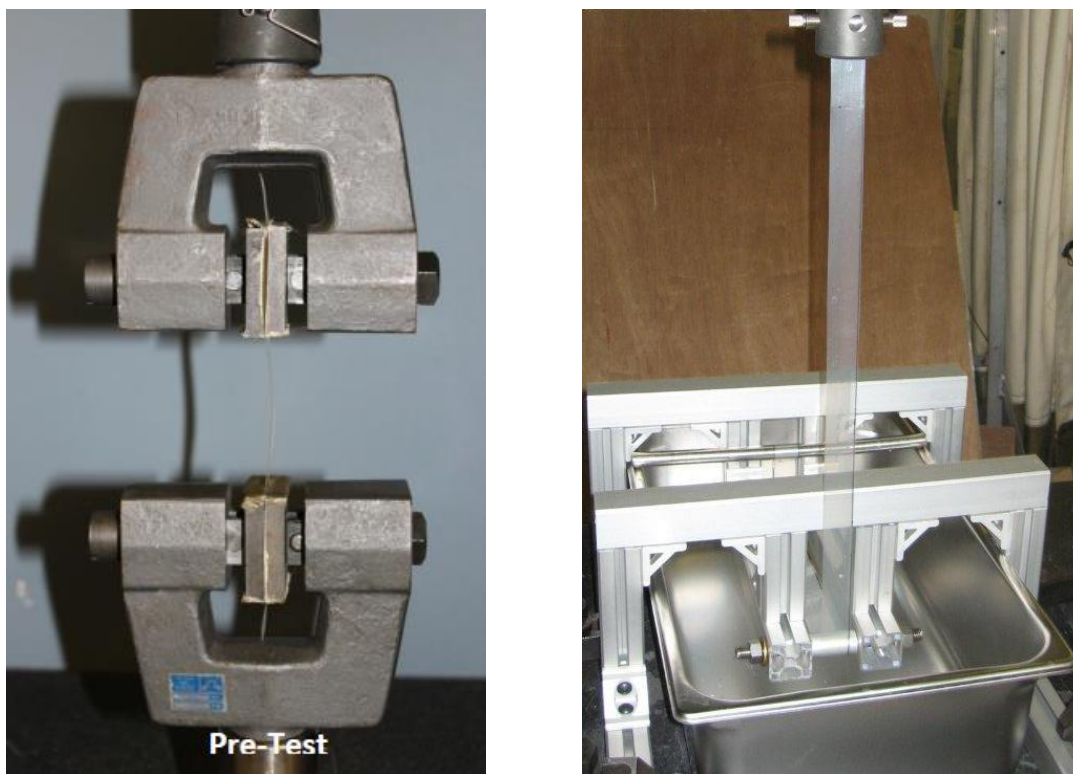


Figure 7: PVOH Tensile Test Setup (left) and Water Exposure Test (right).



Figure 8: Details of PVOH/PHA Weave In-Process.

4.2 FIELD TESTING

The original concept was to construct a cross style decelerator from a single piece of film cut from a wide roll. However, the process of laminating the films reduced the available width of the film roll approximately by half, to 30 inches, and a one-piece film was not possible for this design. It was then necessary to join two pieces of film to create the cross design. A technique was developed to bond the PVOH material together, and in January 2013 a prototype cross style decelerator was constructed. The bulk in the center of the overlapping center area was deemed unacceptable by NSRDEC. The next concept was to use a square parachute design, which is another type of decelerator design in use for some sonobuoys. In March 2013, two prototype decelerators were constructed by NSRDEC using the square parachute design. Figure 9 depicts a prototype constructed from 2-layer, or 4-mil thick PVOH. Two ½-inch wide nylon tapes are sewn across the square film to act as suspension lines and radial tapes.



Figure 9: Square Design for Decelerator.

NSRDEC then produced enough woven material to construct two decelerators of the square type design. A selvage edge was created by tucking the strands back into the weave. Due to loom limits, the decelerators were less than half-scale in size. The decelerators measured 12 inches on each side. In addition to the PHA woven fabric, nylon cordage was used in the construction of the square decelerators. Specifically, two nylon cords were sewn diagonally across each decelerator to form four suspension lines, each extending 36 inches past the decelerator ‘skirt’ and terminating in an eye loop for vehicle attachment. Two test vehicles were constructed from

PVC pipe, each weighing 12 lbs. Figure 10 depicts the test vehicle and packed decelerator. The decelerator was rigged to deploy from the vehicle using a time-delay of 6 seconds after it was dropped. Two airdrop tests were conducted by manually releasing the test vehicles from a helicopter.



Figure 10: Test Vehicle and Decelerator.

5.0 PERFORMANCE ASSESSMENT

5.1 LABORATORY TEST RESULTS

5.1.1 Toxicity Results

The initial toxicity results for the un-laminated film test series indicated there was no difference from the control (0% PVOH) for any of the concentrations. There was between 90-100% survival rates in all the test replicates, showing no toxicity. Additionally, a test was performed with mussel larvae in a 48-hour development test. The same concentrations were used as with the mysids. There appeared to be no toxicity at the higher concentration levels (80 and 100% PVOH, with >90% normal development), however there were issues with the control samples and lower concentrations which showed toxicity. This was due to some contamination issues with the laboratory seawater system, from where the dilution water was obtained. The other tests that were going on for different projects showed toxicity for all their samples. The only non-toxic samples were the high concentration PVOH which had little or none of the dilution water. The contamination was unfortunate, but the results still indicate the PVOH was not toxic at the highest concentration.

Toxicity tests were conducted using the laminated A200 PVOH films, along with repeated tests using the un-laminated film. In this testing, the un-laminated film again displayed no toxicity to mysid, topmelt, sea urchin and mussel species. The laminated film had no toxicity effects on the mysid and topmelt species. However, the sea urchin and mussel tests showed toxicity with both 6-mil and 8-mil laminated sheets. The echinoderm test found the 8-mil thick sheet was more toxic than the 6-mil sheet, with LC₅₀ values of 1.7 and 9.5 mg/L DOC-PVOH, respectively. The mussel test showed similar toxicity for the PVOH 6-mil and PVOH 8-mil with LC₅₀ values of 7.9 and 6.3 mg/L DOC-PVOH, respectively. These data suggest that something related to the lamination process is causing the toxicity. The adhesive used in the lamination process is comprised of a polyurethane resin and ethyl acetate. The ethyl acetate is a known toxicant; however it is released as a VOC during the lamination process. It was determined that residual ethyl acetate from the adhesive used in lamination process was most likely the causative agent. Samples were also analyzed for heavy metals which found concentrations below the toxicity threshold, ruling out metals contamination during the lamination process.

5.1.2 Rate of Dissolution Results

After the project start in January 2012, NSRDEC and Metabolix reviewed commercially available materials. At first look, it was determined the PHA added no benefit when blended with the PVOH for rate of dissolution or for strength. Different grades of PVOH were reviewed. The higher grades provided higher strength, but would neither disintegrate nor dissolve in sea water at 20° C (68° F) within acceptable time durations. A MonoSol formulation called A200 was commercially available and was found to dissolve relatively fast. Figure 11 depicts the

effect of water temperature and the presence of salt on the disintegration time of MonoSol A200 with a film thickness of 50-micron (2-mil). Depending on temperature, disintegration times ranged from 50 seconds to 8 minutes for freshwater and 20 minutes to 3 hours for saltwater.

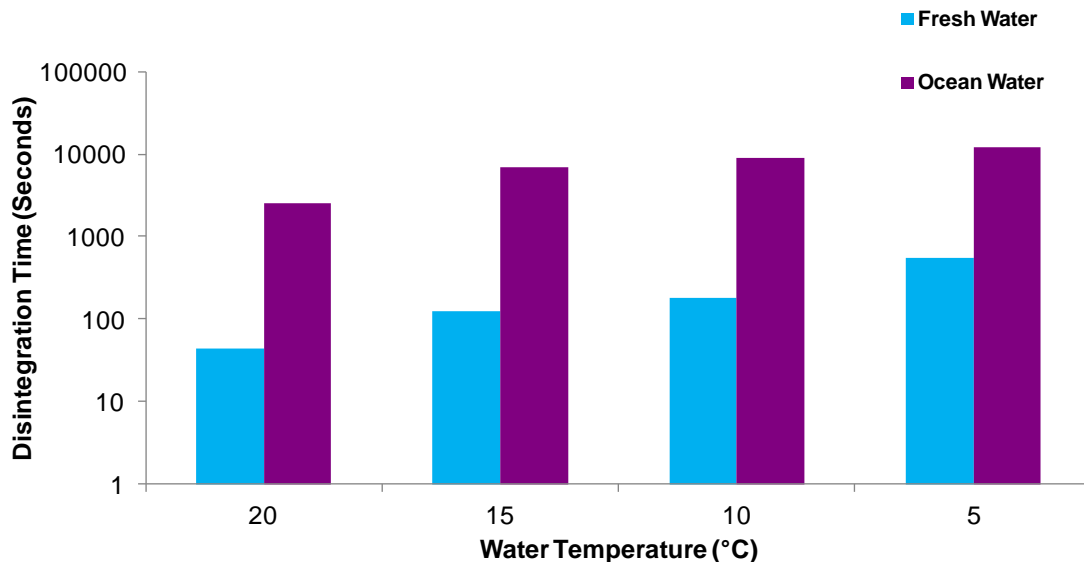


Figure 11: The Effect of Water Temperature and the Presence of Salt on the Disintegration Time of MonoSol A200.

5.1.3 Strength and Elongation Test Results

The PVOH 2-mil thick film tensile strength was measured to be approximately 20 pounds per inch. In order to achieve more strength and longer disintegration time in fresh water, the idea of laminating A200 layers was formed. After some laboratory experimentation in mid-2012, results indicated a laminated film of A200 layers would have the same basic tensile strength as the nylon cloth counterpart currently in use (85 pounds per inch according to the cloth specification PIA-C-7350 for Type I nylon cloth), and would have a dissolution time in the timeframe required to withstand rain exposure during descent, yet meet the goal to eliminate hazards to marine life. Another idea, to apply a water protective coating to the PVOH was explored but dismissed as impractical. NSRDEC found a commercial company capable of laminating the A200 and rolls of 2-layer (4-mil), 3-layer (6-mil), and 4-layer (8-mil) films were delivered in late 2012 to NSRDEC.

Initial tensile testing indicated the mechanical strengths on 1-inch wide film samples of the 4-mil, 6-mil, and 8-mil thick PVOH samples were 50 pounds, 71 pounds, and 86 pounds respectively at room temperature under dry conditions. These samples were tested in the roll direction of the material. During decelerator prototyping, the 8-mil thick film was deemed too stiff. Additional tensile tests were conducted on the 6-mil thick film at NAWCWD. Samples cut from the transverse direction, or across the width of the roll, were also tested. The results of 6

tests in each direction are depicted in Figure 12. A slight difference in strength exists according to orientation. It was also determined the elongation properties are different than for nylon cloth. The film exhibits relatively low elongation until a threshold point is achieved, around 50 pounds per inch. After that the film exhibits very high elongation with strain hardening until reaching the ultimate failure load.

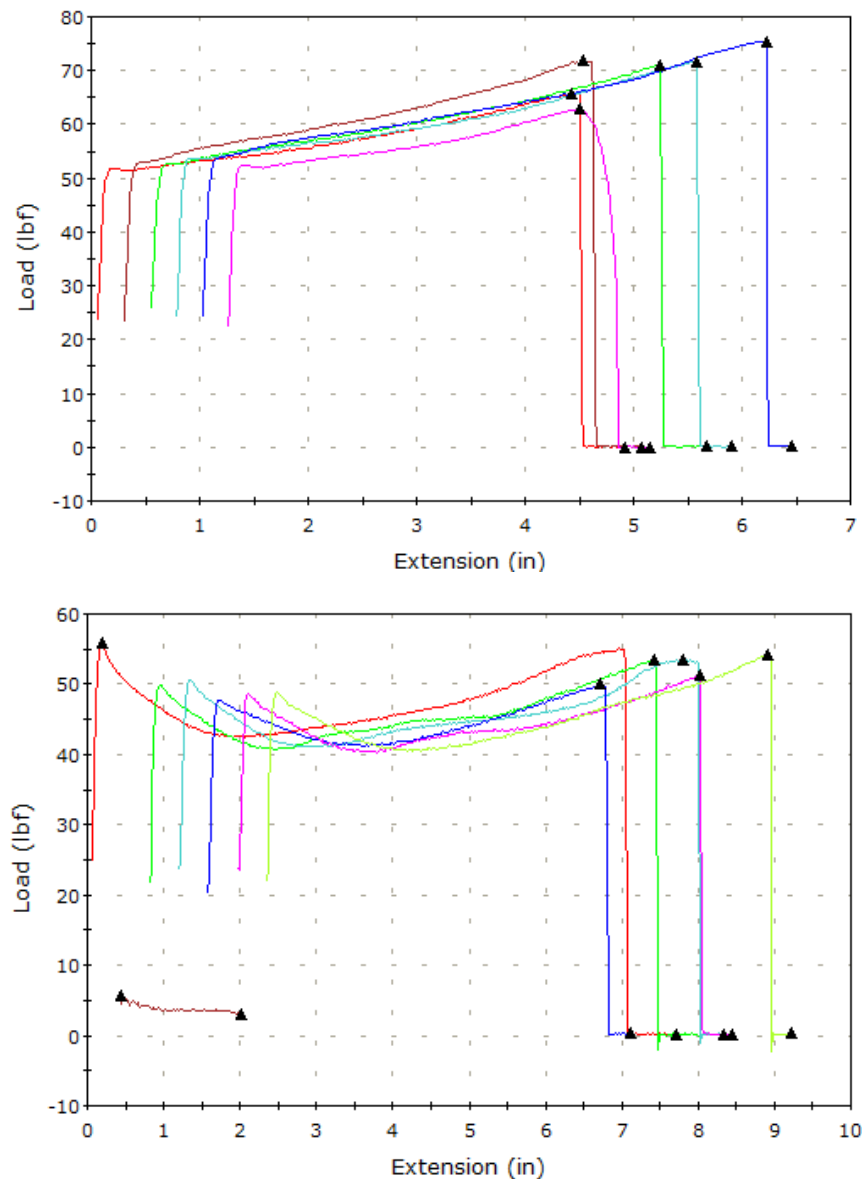


Figure 12: Tensile Test Results of A200 6-mil Film Samples in Lengthwise (Upper) and Transverse (Lower) Rolled Directions.

For both directions tested, the elongation was approximately 5% at the threshold load of 50 pounds per inch. After the threshold load, continued load testing resulted in elongations between 150% and 210% at ultimate failure load. For nylon parachute cloth, the elongation is nearly

linear with loading, with the maximum elongation typically occurring in the 30% to 40% range. Thus the film exhibits a much higher stiffness, 5% compared to 30-40%, in its useful load range.

For the water spray testing, the load was held until the sample broke. The intention was to hold the load for 10 minutes and then determine the breaking strength. However, the sample broke well before the allotted time. Figure 13 depicts the results of one sample. For this sample, the material reached a yield point at approximately 35 seconds, and then subsequently broke just after 55 seconds. A total of six samples were tested with this method, all with similar results. Another set of six tests was conducted using a 10-pound constant load, and the point in time in which yield occurred extended to an average of 1 minute, with the breaking point averaging 4 minutes. Raw data for the strength and water exposure testing is provided in Appendix [B].

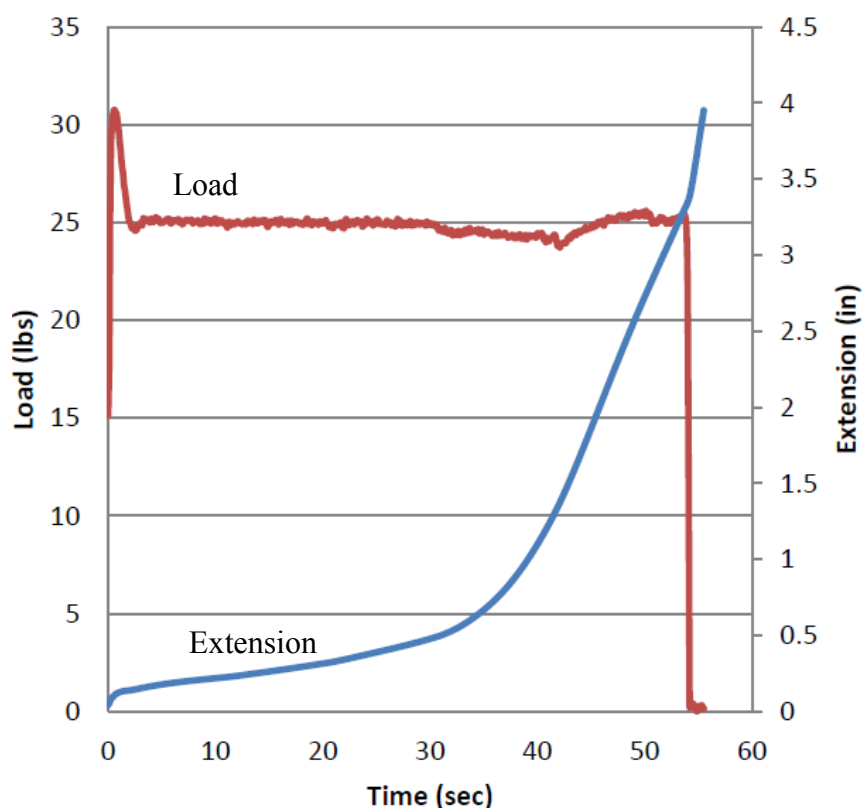


Figure 13: Effect of Water Exposure on Film Sample Held with 25-Pound Load.

Water exposure tests conducted at NSRDEC showed similar results for room temperature water. NSRDEC conducted a cool water exposure test, with a water temperature of approximately 50° F. The sample held for the duration of the two-minute test, but with significant elongation.

The A200 PVOH material modulus versus temperature was also explored in laboratory testing. The modulus test results indicated stiffness increases significantly as temperature decreases below 20° C (68° F).

Strength tests were conducted on the PVOH/PHA composite weave, which indicated the PVOH material was breaking prematurely, thus reducing the overall strength of the weave. NSRDEC then conducted a second weaving trial, utilizing solely the PHA slit film material. Strength testing was conducted on the new weave, and the results indicated a material strength of approximately 45 pounds per inch, which is below the desired strength. Average air permeability was also determined for the new weave and determined to be approximately 30 cubic feet per minute per square foot of surface area.

5.2 FIELD TEST RESULTS

A simple inflation shape check on the 4-mil prototype was conducted using a fan, as shown in Figure 14. As depicted, some asymmetry and ‘dimpling’ can be seen in the inflated shape.



Figure 14: Simple Inflation Test of Prototype PHA Decelerator.

Another prototype was constructed using the 3-layer, or 6-mil thick PVOH. The decelerator was folded into a deployment sleeve made of mesh (Figure 15). Due to the film stiffness being greater than the stiffness of nylon cloth, the prototype decelerator required greater volume and would not fit into the parachute compartment. Another observation regarding stiffness was the effect of cold temperature. When exposed to cold air (30°-40° F), the material became

alarmingly stiff, causing concern for deploying a cold parachute. This design was considered not to be feasible for the application.



Figure 15: Folded 6-Mil Thick PVOH Film Decelerator.

The woven PHA material is much closer to the nylon cloth it is replacing in terms of thickness and flexibility, and is greatly improved compared to the multi-layer PVOH film previously developed. Using the woven PHA scaled decelerators, two tests were conducted in 2013 from an altitude of 1100 feet above ground level. The NSRDEC estimated velocity of the free-falling vehicles at the time the decelerators deployed and inflated was approximately 150 miles per hour. Both tests were successful. Post-test photographs of the decelerators are shown by Figures 16 and 17. The 1/2-inch wide nylon tape used to attach the cloth to the test vehicle, acting as suspension lines, is not biodegradable.



Figure 16: Post Test Photograph of Top Surface of Square Decelerator.



Figure 17: Post Test Photograph of Under Surface of Square Decelerator.

6.0 IMPLEMENTATION ISSUES

The un-laminated PVOH shows promise in terms of dissolution, biodegradability, and toxicity. However, the initial parachute design would require further development to improve strength and pliability, especially in wet or highly humid environments. Key concerns for the multi-layered PVOH film are strength, performance in a rain environment, flexibility at cold temperature, required packing volume, and possible toxicity. Unknowns are effects of long-term humidity exposure during the 5-year storage.

The PHA weave alleviates the above concerns to a degree but needs further development to become a replacement for the nylon cloth currently in use for sonobuoy decelerators. The PHA material is not dissolvable and requires 4 to 12 months to biodegrade in marine environments, depending on temperature and microbial population. While the airdrop tests were conducted with scaled decelerators and payloads and at relatively low velocities and altitudes, the results are promising. A full-scale PHA woven decelerator would likely pack into the allotted volume within the sonobuoy. Production of a full-size decelerator and a packing trial are needed for validation. Additional tests are needed to verify it can meet all the requirements as a replacement for nylon cloth. Work remains to develop a material specification for the new weave. Commercial production weaving development is also required. Long-term sources of the PHA film/strip material need to be verified.

The efforts of this project have resulted in an understanding of the behavior and performance of several types of PVOH and PHA materials in various environmental conditions and how this knowledge can be used to gain further success. A clear and effective testing protocol has been developed which will provide a high level of confidence in the performance of any candidate material for the development and demonstration of a sonobuoy decelerator. Although the prototypes tested at this point have not resulted in a successful sonobuoy decelerator, the knowledge gained will be critical to the future projects.

7.0 REFERENCES

1. AIB-VINCOTTE International. “Certificate for Awarding and Use of the “OK Biodegradable Water” Conformity Mark”, Certificate No. O12-1005-A, Brussels, **2012**.
2. Thellen, C.; Coyne, M.; Froio, D.; Auerbach, M.; Wirsén, C.; Ratto, J. “A Processing, Characterization, and Marine Biodegradation Study of Melt-Extruded Polyhydroxyalkanoate (PHA) Films”, *Journal of Polymers and the Environment*, 16, **2008**, pp 1-11.
3. Bilkovic, D.; Havens, K.; Stanhope, M.; Angstadt, K. “Use of Fully Biodegradable Panels to Reduce Derelict Pot Threats to Marine Fauna”, *Conservation Biology*, 26, 6, **2012**, pp 957-966.

APPENDICES

Appendix A: Points of Contact

Point of Contact	Organization Address	Phone Email
Warren Ingram	Naval Air Warfare Center Weapons Division, Code 466100D, 1 Administration Circle Stop 6206, China Lake, CA 93555	(760) 382-7321 warren.ingram@navy.mil
Dr. Robin Nissan	Department of Defense Environmental Security Technology Certification Program, 4800 Mark Center Drive, Suite 17D08, Alexandria, VA 22350	(571) 372-6399 robin.a.nissan.civ@mail.mil

Appendix B: Strength Test Results for 6-mil Laminated PVOH

Note: all samples cut to a 1-inch width

RAVEL STRIP STRENGTH TEST (ALONG MATERIAL ROLL WIDTH)

Description: Tension sample to breaking load with samples set up taut with 3" gap between jaws. Sample was cut along material roll width.

Date: 03/27/13

Temp: 76°C

Humidity: 13%

SAMPLE	LOAD (LBS) <i>1st Peak</i>	BREAKING STRENGTH (LBS) <i>2nd Peak</i>	NOTES
1-1 (specimen1)	55.80	55.09	
1-2 (specimen3)	49.82	53.49	Jaws not tightened on Specimen 2. Same sample used for Specimen 3.
1-3 (specimen4)	50.64	53.47	
1-4 (specimen5)	47.78	50.00	
1-5 (specimen6)	48.67	51.20	
1-6 (specimen7)	48.87	54.12	
AVERAGE	50.26	52.90	

RAVEL STRIP STRENGTH TEST (ALONG MATERIAL ROLL LENGTH)

Description: Tension sample to breaking load with samples set up taut with 3" gap between jaws. Sample was cut along material roll length.

Date: 03/27/13

Temp: 76°C

Humidity: 13%

SAMPLE	LOAD (LBS) 1 ST PEAK	BREAKING STRENGTH (LBS) 2 ND PEAK	NOTES
2-1 (specimen1)	51.86	65.85	
2-2 (specimen2)	52.69	71.81	
2-3 (specimen3)	52.51	71.13	
2-4 (specimen4)	53.77	71.74	
2-5 (specimen5)	53.82	75.43	
2-6 (specimen6)	52.49	62.87	
AVERAGE	52.86	69.81	

CREEP AND RECOVERY TEST @ 25-lbs for 1-min

Description: Tension sample to 50% average breaking strength, determined above as 25-lbs, and hold for 1 minute. Samples were cut along width of roll, and set up with 3" gap between jaws. Length measurements were taken before test, 1 minute after, 5 minutes after, and 1 hour after to measure recovery. Samples were then taken to yield.

Date: 03/28/13

Temp: 75°C

Humidity: 13%

SAMPLE	LENGTH @ START (IN)	LENGTH @ 1 MIN (IN)	LENGTH @ 5 MIN (IN)	LENGTH @ 1 HR (IN)	BREAKING LOAD (LBS)	NOTES
3-1 (specimen1)	9	$9 \frac{3}{32}$	$9 \frac{3}{64}$	$9 \frac{1}{64}$	57.87	
3-2 (specimen2)	9	$9 \frac{1}{8}$	$9 \frac{1}{16}$	$9 \frac{1}{64}$	57.81	
3-3 (specimen3)	$8 \frac{63}{64}$	$9 \frac{5}{64}$	$9 \frac{1}{32}$	9	54.59	
3-4 (specimen4)	9	$9 \frac{3}{32}$	$9 \frac{3}{64}$	$9 \frac{1}{64}$	54.07	
3-5 (specimen5)	9	$9 \frac{1}{8}$	$9 \frac{1}{16}$	$9 \frac{1}{32}$	51.61	
3-6 (specimen6)	9	$9 \frac{1}{8}$	$9 \frac{3}{64}$	$9 \frac{1}{64}$	52.85	
AVERAGE	9.00	9.11	9.05	9.02	54.80	

LOSS IN STRENGTH DUE TO WATER EXPOSURE @ 25 POUNDS HOLD

Description: Tension sample to 50% average breaking strength, determined above as 25-lbs, and hold for 5 minutes. Using a spray bottle, with nozzle about 3-4" away from sample, spray each side of sample once every 10 seconds while under load. The water in the spray bottle was at room temperature. Samples were cut along width of roll, and set up with 3" gap between jaws. Towels and plastic sheeting were placed around the Instron and fixtures to protect them from the water spray.

Date: 04/02/13

Temp: 75°C

Humidity: 13%

SAMPLE	EST. TIME TO YIELD	EST. TIME TO BREAK	NOTES
5-1 (specimen1)	~36 sec	~58 sec	
5-2 (specimen2)	~32 sec	~51 sec	
5-3 (specimen3)	~34 sec	~37 sec	
5-4 (specimen4)	~34 sec	~41 sec	
5-5 (specimen5)	~34 sec	~52 sec	
5-6 (specimen6)	~34 sec	~54 sec	
AVERAGE	~34 sec	~49 sec	

LOSS IN STRENGTH DUE TO WATER EXPOSURE @ 10-LBS

Description: Tension sample to 50% average breaking strength, determined above as 10-lbs, and hold for 5 minutes. Using a spray bottle, with nozzle about 3-4" away from sample, spray each side of sample once every 10 seconds while under load. The water in the spray bottle was at room temperature. Samples were cut along width of roll, and set up with 3" gap between jaws. Towels and plastic sheeting were placed around the Instron and fixtures to protect them from the water spray.

Date: 04/02/13

Temp: 75°C

Humidity: 13%

SAMPLE	EST. TIME TO YIELD	EST. TIME TO BREAK	NOTES
6-1 (specimen1)	~50 sec	~ 208 sec	
6-2 (specimen2)	~50 sec	~250 sec	
6-3 (specimen3)	~50 sec	~243 sec	
6-4 (specimen4)	~50 sec	~257 sec	
6-5 (specimen5)	~50 sec	~230 sec	
6-6 (specimen6)	~50 sec	~270 sec	
AVERAGE	~50 sec	~243 sec	